UTILIZATION OF FLY ASH IN STRUCTURAL AND DECORATIVE CERAMIC PRODUCTS

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INTRODUCTION AND BACKGROUND

The main objective of this study is to promote the use of fly ash from electric power plants in Illinois in the manufacture of bricks. Fly ash that is produced during the burning of coal represents a continuing disposal problem and thus a disincentive to coal's use. Each year, approximately 5 X 10^6 metric tons of fly ash are produced from burning Illinois coals. Use of brick clays for ceramic products in the Illinois area amounted to about 0.5 X 10^6 metric tons in 1994. If significant amounts of fly ash were used in the manufacture of fired-clay products such as brick, the fly ash disposal problem would be reduced, a valuable construction product would be created, and mining of brick clays would be slowed. Furthermore, the clay minerals in the green bricks are dehydroxylated during the firing process. Fly ash already has been through dehydroxlyation, therefore this energy for dehydroxylation is "saved" during brick manufacture. Six tasks were defined to meet our objectives: 1) manufacture bricks that contain 20 wt% or more of fly ash under normal plant-scale conditions; 2) measure the firing characteristics of mixtures created by using extremes in chemical composition of Illinois fly ashes and brick clays and shales; 3) from those measurements, derive equations that predict the firing characteristics of any mixture of clay and fly ash; 4) optimize mixtures of brick clays with sources of fly ash near existing ceramic plants; 5) perform tests to determine the leachability of toxic constituents, if any, from the bricks; and 6) integrate the results of tasks 1 and 2 with preliminary engineering and market assessments to evaluate the feasibility of large-scale use of fly ash in fired-clay products.

Although general principles guiding the selection of raw materials for fired-clay products have been known for many years (Grim, 1962; Burst and Hughes, 1994), the complexity of the firing reactions suggested the need for improved methods (Hughes, 1993) of predicting the firing behavior of bricks and related products. This need is emphasized by our plant-scale experiments with Colonial Brick Company in Cayuga, Indiana. Because we lack adequate methods for prediction, we were obliged to resort to trial-and-error methods for our first plant-scale test. The improvement of methods for predicting the properties of fired fly ash, shale, and underclay mixtures is now possible, and an approach based on mineral content is expected to provide significant improvements in accuracy of prediction.

An improved method for the prediction of coal ash fusion temperature is an important outcome expected from this study. Laboratory methods for the estimation of coal ash fusion temperature are the same as those for testing ceramics. As for ceramic products, the methods used to predict coal ash fusion temperatures are notoriously inaccurate because they are based on chemical analyses. For the ceramic and the coal ash fusion tests, we suggest that equations based on mineralogical composition will yield improved accuracy and precision. A mineralogical basis for prediction also should elucidate the underlying mechanisms that cause problems and suggest solutions to those problems.

The manufacturing process at most brick plants is similar. Clays are blended in a crusher, pulverized, and water and dispersant are added in a pugmill to produce a plastic clay that can be extruded. The preferred raw materials for these fired-clay products occur as underclays and roof shales associated with coals. They contain variable amounts of three basic groups of minerals: 1) relatively low-melting-point illite, mixed-layered illite/smectite (I/S), and chlorite; 2) refractory kaolinite and mixed-layered kaolinite/expandables (K/E); and 3) somewhat refractory quartz. Common red-firing roof shales generally contain nearly ideal amounts of group 1 and 2, and adequate firing characteristics are obtained by blending clay-rich shale zones with sandier, quartz-rich zones. The mixture must contain enough clay minerals for adequate plasticity, and enough coarse grains to insure access of air so that the core of the brick is completely oxidized in the shortest possible time during firing.

Many of the shales immediately above coals (roof shales) in the Illinois Basin are nearly ideal raw materials. Their progressive change in grain size from smaller at the base to larger at the top, makes blending for plasticity and firing rate possible. Many underclays below Illinois coals are fireclays, which, unlike shales, contain more kaolinite and significant amounts of K/E. This K/E gives special properties to fired-clay products because it is composed at the atomic scale of a 2:1 clay mineral layer that melts at relatively low temperatures and a 1:1 layer that is refractory. Quartz also can have special properties during firing. Quartz acts as a framework grain in normal shale and fireclay bricks, but at high enough temperature, it can melt and act as a bonding agent. For these reasons, predictive equations must be made with different groupings of mineralogical factors.

Background information on clays for bricks and similar ceramic products is summarized in Hughes (1993). Slonaker (1977) showed that acceptable bricks were produced from feeds of 72% fly ash, 25% bottom ash, and 3% sodium silicate. A general discussion of the properties of fly ash that are important to its use in fired-clay products can be found in Kurgan, Balestrino, and Daley (1984). They reported that the high alkalinity of fly ash from Illinois could improve dispersion of the clay body during mixing and extrusion of bricks. Talmy *et al.* (1995) described two approaches for using 100% fly ash plus additives to make bricks.

The development and use of leaching tests for the measurement of environmental impacts of coal combustion residues was reviewed in Dreher, Roy, and Steele (1993). Improved methods for the mineralogical characterization of coal samples and coal combustion wastes have been described recently by Kruse *et al.* (1994) and Moore, Dreher, and Hughes (1995). Characterization methods for clay minerals are described in Hughes and Warren (1989) and Moore and Reynolds (1989).

If successful, the results obtained from this project should lead to an attractive solution, from an environmental and economic standpoint, for the recycling of fly ash to high-value marketable products. Success also could revitalize the ceramics industry in Illinois, an industry that has been in decline for several years. Finally, high-calcium fly ashes may be useful for capture of sulfur that volatilizes from brick clays during firing.

EXPERIMENTAL PROCEDURES

Brick manufacturing tests were made using fly ash from Illinois Power Company's Wood River Power Plant. Colonial Brick Company conducted a manufacturing run of about 5,000 bricks without fly ash and a similar number with about 20% fly ash added to the normal clay. A batch of bricks of each of the two compositions was fired side-by-side in the kiln and tested for standard market specifications, *i.e.*, samples of the bricks with and without fly ash were taken during firing to provide a measure of "clearing" or time required to completely oxidize the core of the bricks. Water absorption tests and of color determinations also were made by Colonial Brick on the fired products. These proved acceptable to them.

Mineralogical characterization was made by X-ray diffraction (XRD), X-ray fluorescence, instrumental neutron activation analysis, and a step-wise dissolution in 2N HCl with inductively coupled plasma (ICP) analysis of the supernates and XRD of the solids. The X-ray diffractometer was a Scintag® unit that used a Cu tube, a θ/θ goniometer, a 12-position sample changer, a liquid N_2-cooled germanium detector, and computer controls and peak deconvolution programs. The XRF spectrometer was a Rigaku® wavelength-dispersive model that has a chromium radiation source and a 6-position sample changer. The ICP spectrometer was a Jarrell-Ash Model 1155V vacuum spectrometer equipped with 35 element channels. Instrumental neutron activation analysis was accomplished by irradiating solid samples in a neutron flux at the University of Illinois Advanced TRIGA MARK II reactor. After suitable decay times, gamma-ray spectra for various elements in the irradiated sample were recorded by a multi-channel analyzer. For step-dissolution experiments, about 1 gm samples were ground in a McCrone micronizer®, ultrasonically dispersed in 50 mL of H_2O, and added to 550 mL of 2N HCl. Stirred, 40 mL aliquots were extracted from the suspension at selected intervals for up to a month, *e.g.*, 2 hr, 4 hr, 8 hr, etc. To increase solubility, one fireclay sample was heated to 500°C to dehydroxylate most of its kaolinite and K/E.

Leaching procedures developed by Dreher *et al.* (1988, 1989) are being used to determine the extent to which constituents of environmental concern might leach from bricks exposed to weathering. Batch extraction and wet-dry leaching experiments, in which the substrate is exposed to deionized water for a given time period, are being conducted on crushed and whole bricks. To simulate exposure in a building, five faces of the bricks are protected from leaching by application of an epoxy coating. Batch extraction experiments are being conducted at a solution-to-solid ratio of 4:1 for periods of 3, 10, 30, 90, and 180 days. Each solid was analyzed chemically and mineralogically prior to extraction and leaching experiments, and the solids from the 180-day extraction will be analyzed mineralogically.

Estimates of the composition of Illinois fly ashes were obtained from Moore, Dreher, and Hughes (1995) and by calculation from the composition of coals reported by Demir *et al.* (1994). These two sources of fly ash chemical composition were plotted in various ways to find the range of composition available as a replacement for clays in bricks (Figs. 1 and 2). Results from laboratory and plant tests will be analyzed by factorial analysis and regression analysis to obtain equations that measure the effect on fired properties of additions of each of the basic components from the raw materials.

RESULTS AND DISCUSSION

Plant-scale tests. The results of the production run were somewhat unexpected. During firing, we expected the fly ash to increase gas movement into and out of the bricks, but the reverse occurred. Essentially, the fly ash decreased the rate of oxidation. The bricks with fly ash also had noticeably more "scumming," which also was unexpected. This scumming causes a white to cream-colored dusting on the outside of the bricks and is mostly due to the migration of calcium sulfates to the surface during drying, firing, or both. We will attempt to confirm this assumption with chemical analyses. The problem can be corrected by adding barium carbonate, or possibly by moistening the fly ash and precipitating the salts, or it may be possible to simply select a fly ash with a smaller calcium sulfate content. A benefit resulting from the effect of fly ash on gas permeability was the lack of an expected increase in water absorption by the products. In general, the bricks from the manufacturing run were within local and regional market specifications. However, the scumming reduces their marketability.

On a matter of importance to the plant operator, the amount of dust associated with unloading fly ash at Colonial Brick was an unexpected problem that must be solved because of environmental regulations. It may be possible to wet the ash at the power plant or use pneumatic facilities at the brick plant.

Characterization of materials. The mineralogical and chemical analyses of clay and fly ash samples are given in Tables 1 and 2. The shales used are typical red-firing Pennsylvanian shales, which are common as the roof shale of most coals. At Colonial Brick Company's pit, about 30 ft of roof shale overlies a 6-12 in carbonaceous or coaly zone, which overlies about 6 ft of fireclay. The coaly zone may be equivalent to the Colchester (No. 2) Coal. Our second-year collaborator, Marseilles Brick Company, mines shale and fireclay from different pits. The shale is middle or upper Pennsylvanian and the fireclay occurs in the Cheltenham Formation, immediately below the underclay of the Colchester Coal.

For the approximately 25,000 samples of ceramic clays that have been collected since 1930 at the Illinois State Geological Survey, a database was constructed for this study. This database lists locations and material types. The location and selection of fly ash standards proved more difficult than the selection of clays. Data for each of the coals in Demir *et al.* (1994) were modified in an Excel© spreadsheet to estimate the chemical composition of fly ash from each of these coals (Figs. 1 and 2). The chemical composition of 8 fly ash samples that were part of the characterization study by Moore, Dreher, and Hughes (1995), and the chemical analyses of the fly ash and brick clays used in this investigation, were added to the spreadsheet and plotted (Figs. 1 and 2).

Most fly ashes contain more iron and calcium than brick clays (Figures 1 and 2). Because they were fused, the fly ashes may differ in the degree to which chemical constituents are segregated between phases and glass. However, to represent the range of available materials, we selected fly ash compositions that were relatively rich in: 1) $SiO_2 + Al_2O_3$, 2) Fe_2O_3, and 3) CaO. Differences in the contents of these constituents represent the important compositional variation for most Illinois fly ashes. In order to better understand the relationship between the chemical and mineralogical contents of coals, we plan to calculate regression equations of the chemical and mineralogical contents of the Illinois Basin Coal Sample Program (IBCSP) coals (Kruse *et al.*, 1994) and use those equations to estimate the mineralogical content of the 34 commercial coals of Demir *et al.* (1994).

Figure 2 shows that $SiO_2:Al_2O_3$ is nearly constant. This ratio ranges from 1.9 to 3.6 with a mean of about 2.5 in the data set of Demir *et al.* (1994), and a range of 2.3 to 3.9 with a mean of about 2.5 in the data of Moore, Dreher, and Hughes (1995). The differences in the contents of CaO, Fe_2O_3, K_2O, and Na_2O in fly ashes and brick clays account for most of the significant variation in these materials. For purposes of selecting standards for optimization studies, the fly ash used in production runs this year (Table 2) can be used to represent fly ashes that are rich in SiO_2 and Al_2O_3. Samples 2 and 8 from the set of fly ashes analyzed by Moore, Dreher, and Hughes (1995) can be used to represent CaO-rich and Fe_2O_3-rich types, respectively. We selected and analyzed two standard optimization clays from Marseilles Brick Company.

Step-dissolution analysis and optimization. We believe that the solution to the problem of predicting the firing behavior of mixtures of materials depends on the accurate measurement of the major and minor mineral phases that make up a material. For unfired materials, XRD analysis of the mineral content is the technique of choice. However, some of the clay minerals are difficult to determine accurately, and we have chosen step-dissolution methods with ICP and XRD analyses to improve the determinations (Cícel and Komadel, 1994; Moore, Dreher, and Hughes, 1995). Figures 3 and 4 show the results of step-dissolution analyses of shale samples used at Colonial Brick Company. Because chlorite has two octahedral sites that can be occupied by Al, Fe, or Mg, it is the most difficult non-mixed-layered clay mineral to determine by XRD. In addition, of the minerals of concern in the shale, it is the most soluble in HCl. Therefore, XRD analyses of the solid fraction of the samples showed a decrease in chlorite content as time of reaction in 2N HCl increased (Fig. 3). Similarly, results of elemental analyses of the supernates recorded the increase in chlorite-forming elements with increased reaction time (Fig. 4). These plots of elemental concentration versus time can be used to calculate a structural formula of the chlorite in the sample and will make the optimization equations more accurate. The formula for chlorite derived from Fig. 4 is $Al_{1.6}Fe_{2.9}Mg_{1.4}Mn_{0.1}Si_{3.0}Al_{1.0}O_{10}\cdot(OH)_8$.

After chlorite has been dissolved, step dissolution analysis of fireclays and shales becomes difficult because of the low solubility of the minerals remaining in the system. There are no easily dissolved minerals in fireclay and fly ash samples, therefore this becomes a major analytical problem. For fireclays, only 3 to 6% of the untreated sample was dissolved. A pre-treatment at 500°C increased the solubility of kaolinite and K/E, and gave meaningful estimates of the composition of those phases. To improve the method, it appears that we will have to grind the samples longer, leave them in acid longer, increase the strength of the acid, increase the temperature, or use some combination of these methods to dissolve all the amorphous material from fly ash samples.

Future studies. Recent studies of the firing behavior of bricks and related materials suggested that we may need to expand the number of tests used to measure fired-clay properties. This expansion will add tests for shrinkage, rate of burnout, hardness, strength, pyrometric cone equivalent (PCE), color, and water adsorption. Many of these determinations can be done on the samples used for PCE analysis and most of the tests would increase the analytical costs only moderately. The amounts of CaO, $CaSO_4$, and Fe_2O_3 (from pyrite and marcasite) in some fly ashes are too large to be used for manufacture many ceramic products. The excess calcium from these sources can be corrected for by adding water in the cooling part of the firing cycle. This method was used in the manufacture of bricks known as "Chicago Commons." The scumming problem from calcium sulfates in fly ash may be solved by adding 5-15% water to the fly ash and eliminating it by processing fly ashes into various fractions. Both the color and lower melting point caused by high levels of Fe_2O_3 are best adjusted for by increasing the quartz and/or kaolinite content of the clay-shale. Problems with SO_2 emissions are common in brick production, and we plan to test high-Ca fly ash for its ability to capture sulfur from the clays during firing.

SUMMARY AND RECOMMENDATIONS

Additions of fly ash to bricks at the 20% level in plant-scale tests increased scumming and "burn-out" problems, but, contrary to our expectations, failed to increase water absorption. Although these problems are not expected to cause insurmountable difficulties, better characterization of the mineralogical composition of fly ashes is needed to find solutions to such problems.

Characterization of the clays used at Colonial and Marseilles Brick Companies showed that they are typical of the Pennsylvanian-age clays associated with coals of the Illinois Basin. A computer database of approximately 25,000 ceramic clays of Illinois was constructed, and the database of chemical composition of marketed Illinois coals reported in Demir *et al.* (1994) was processed to estimate the composition of fly ash that would be produced from burning each of those coals. The chemical composition of the eight fly ash samples from the study of Moore, Dreher, and Hughes (1995) also were added to a composite database. Characterization by XRD, XRF, INAA, and step-dissolution/ICP analyses of the fly ashes, shales, fireclays, green bricks, and fired bricks showed that the fly ashes contained more CaO and Fe_2O_3 than the brick clays. However, there is a wide range of chemical composition and an unknown variation in the mineralogical content of fly ashes. Low solubilities of minerals in fly ashes and fireclays made it difficult to use the step-dissolution method for the mineralogical characterization of those materials. Preheating fireclays to dehydroxylate kaolinite and mixed-layered kaolinite/expandables (K/E) in fireclays and more intense grinding of fly ashes seemed to give adequate step-dissolution results. Environmental leaching studies are being conducted to evaluate the leaching of potential pollutants.

To broaden the comprehensiveness of the fundamental studies, future studies will include determinations of water absorption, shrinkage, rate of burnout, hardness, color, and pyrometric cone equivalent (PCE) on mixtures of fireclay, fly ash, and shale. To reduce SO_2 emissions from brick clays, fly ashes rich in Ca will be tested to determine the amount of sulfur that can be captured during firing. Comparisons between the composition of fly ash calculated from the elemental compositions of coals and the actual fly ash samples and between predicted and actual coal ash fusion temperatures will be made to assess the accuracy of predictive methods from this study.

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Table 1. Mineralogical composition (%) of Colonial Brick and Marseilles Brick clays

Sample	I/S	I	K/E	K	C	Q	Kf	Pf	Cc	Py	Other
sh3521A	10	25	0	8.9	11	39	0.1	5.9	0.0	0.0	
sh3521C	15	19	0	5.7	6.5	47	0.2	6.0	0.0	1.5	
fc3521B	45	10	0	7.8	0.0	34	0.0	1.3	0.0	2.1	
fc3521BR	45	10	0	7.8	0.0	33	0.0	1.3	0.0	3.1	
fc3538A	19	3.4	22	7.6	0.0	44	0.4	0.0	0.0	2.9	
sh3538B	17	18	0	3.1	7.4	48	0.4	5.8	0.0	0.0	
sh3528A	17	16	0	5.3	5.1	47	1.3	8.2	0.0	0.0	
sh3528AR	15	19	0	6.1	7.6	46	0.0	6.8	0.0	0.0	
fc3528B	27	6.9	14	7.6	2.1	37	0.0	1.7	0.8	2.1	
fc3528BR	33	6.4	13	7.0	1.6	34	0.4	1.4	0.8	2.0	
sh3548A	19	21	0.0	4.0	7.7	42	0.8	5.4	0.0	0.0	apatite?
sh3548AR	19	20	0.0	3.9	7.5	44	0.6	5.8	0.0	0.0	apatite?
fc3548B	18	2.5	32	9.0	0.0	33	0.0	0.0	0.4	4.5	
flsh3538E						11					glass, M, H
flsh3538F						12					glass, M, H
shbr3521F	16	19	0.0	5.7	5.8	48	0.2	5.6	0.0	0.0	apatite?
shbr3521G	17	27	0.0	6.5	8.3	36	0.0	4.9	0.0	0.0	apatite?
shbr3521J	15	20	0.0	4.9	7.7	46	0.4	5.3	0.0	0.0	apatite?
shbr3521K	15	19	0.0	4.0	6.4	50	0.7	5.6	0.0	0.0	apatite?
br3521D						25					glass, M, H
br3521E						21					glass, M, H
br3521H						27					glass, M, H
br3521I						28					glass, M, H

Key: Samples 3521, 3538 = Colonial Brick 3/94 and 4/95; samples 3528, 3548 = Marseilles Brick 10/94 and 6/95; I/S = mixed-layered illite/smectite; I = illite; K/E = mixed-layered kaolinite/expandables; K = kaolinite; C = chlorite; Q = quartz; Kf = K-feldspar; Pf = plagioclase feldspar; Cc = calcite; Py-Ma = pyrite-marcasite; M = mullite; H = hematite; R = repeat; sh = shale; fc = fireclay; flsh = fly ash; shbr = unfired brick; br = fired brick; (3521D, E, F, G = bricks with 20% fly ash; 3521H, I, J, K = bricks without fly ash).

Table 2. Chemical composition (%) of Colonial Brick Co. clays, Marseilles Brick Co. clays, and bricks from the manufacturing run at Colonial

Sample	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	Na2O	TiO2	LOI	P2O5	Sr	Ba	Zr
sh-3521A	61.33	17.7	6.52	0.57	1.9	3.09	1.08	0.98	6.44	0.16	0.14	0.53	0.23
shbr-3521C	60.81	17.66	6.47	0.6	1.91	3.07	1.07	0.97	6.82	0.16	0.15	0.54	0.23
sh-3538A	59.96	18.86	6.5	0.39	2.07	3.36	1.04	0.98	6.34	0.17	0.14	0.65	0.13
fc-3521B	57.47	21.37	4.71	1.67	1.47	2.68	0.35	1.1	7.98	0.16	0.25	0.44	0.25
fc-3538C	58.27	21.49	5.06	0.78	1.38	2.35	0.47	1.11	8.15	0.1	0.18	0.41	0.19
fc-3528A	59.22	26.18	1.99	0.31	0.5	0.96	0.04	1.27	8.93	0.06	0.16	0.09	0.29
sh-3528B	66.38	16.81	4.96	0.32	1.95	3.22	1.3	1.03	3.52	0.14	0.10	0.43	0.27
grbr1-3521F	61.09	18.18	6.12	0.88	1.78	2.83	1.04	1.01	6.27	0.17	0.20	0.62	0.17
grbr2-3521J	62.81	17.02	5.89	0.56	1.75	2.74	1.02	0.98	6.52	0.17	0.19	0.46	0.18
br1-3521D	64.71	19.71	6.68	0.86	1.95	3.08	1.08	1.07	0.13	0.18	0.21	0.69	0.18
br2-3521H	66.44	18.61	6.39	0.65	1.96	3.05	1.07	1.04	0.19	0.17	0.16	0.62	0.19
br2R-3521H	66.37	18.51	6.42	0.64	1.94	3.04	1.09	1.04	0.21	0.18	0.18	0.56	0.20
flsh1-3538E	54.5	25.5	6.39	2.55	1.29	2.22	1.13	1.34	3.42	0.19	0.75	1.27	0.24
flsh2-3538F	54.73	25.42	6.38	2.54	1.3	2.22	1.11	1.35	3.18	0.19	0.75	1.25	0.20

Key: Samples with clay numbers 3521 and 3538 are from Colonial Brick Co.; 3528 are from Marseilles Brick Co.; grbr1 = unfired brick with 20% fly ash; grbr2 = unfired brick without fly ash; br1 = fired brick with 20% fly ash; br2 and br2R = fired brick samples without fly ash; flsh1 and flsh2 are duplicate fly ash samples.

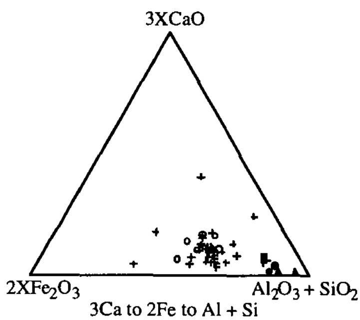

Figure 1. Triangular plot of $CaO:SiO_2+Al_2O_3:Fe_2O_3$. Symbols: + = data set of Demir et al. (1994); O = data set of Moore, Dreher, and Hughes (1995); ● = Colonial Brick Company's shale and fireclay; ▲ = Marseilles Brick Company's shale and fireclay; ■ = fly ash used for tests at Colonial Brick.

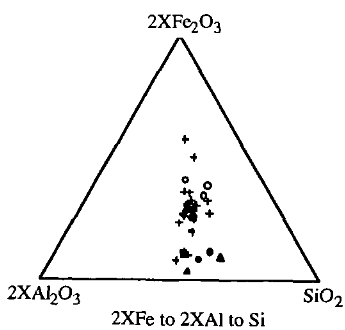

Figure 2. Triangular plot of $Fe_2O_3:Al_2O_3:SiO_2$. Symbols: + = data set of Demir et al. (1994); O = data set of Moore, Dreher, and Hughes (1995); ● = Colonial Brick Company's shale and fireclay; ▲ = Marseilles Brick Company's shale and fireclay; ■ = fly ash used for tests at Colonial Brick.

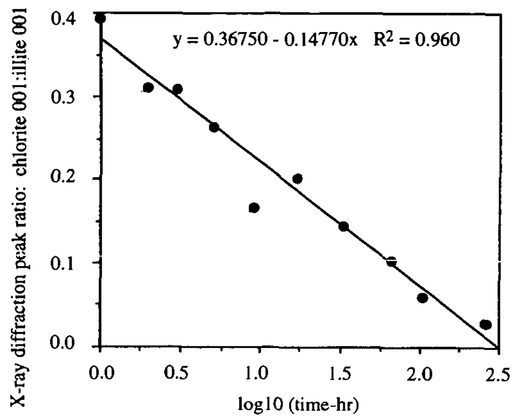

Figure 3. Plot of the XRD peak intensity ratio of the chlorite 001 to the illite 001 peaks from solid samples. This plot shows the dissolution of chlorite in 2N HCl with time. (See figure 4 for a plot of the dissolved species from chlorite.)

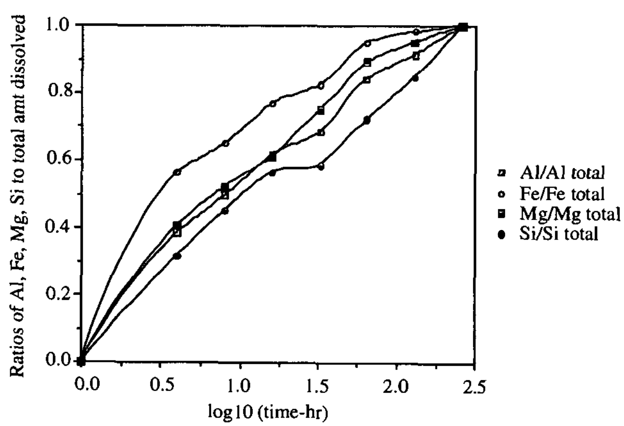

Figure 4. Plot of the ratio of Al, Fe, Mg, and Si ions in solution to the total amount of that constituent in solution at the end of the experiment. This plot shows variation in Al and Si versus Fe and Mg solution rate, which reflects the lower solubility of the tetrahedral sheet of the chlorite structure. The concentration when all chlorite has been dissolved gives a structural formula for the chlorite, *i.e.*, $Al_{1.6}Fe_{2.9}Mg_{1.4}Mn_{0.1}Si_{3.0}Al_{1.0}O_{10}{\bullet}(OH)_8$.